PB86-118585

Validation of Soxhlet Extraction Procedure for SW-846

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-118585

EPA/600/4-85/073
October 1985

VALIDATION OF SOXHLET EXTRACTION PROCEDURE FOR SW-846

by

Larry C. Michael, M. Arthur Moseley, John W. Hines
and Edo D. Pellizzari
Research Triangle Institute
Post Office Box 12194
Research Triangle Park, North Carolina 27709

Contract No. 68-03-3099
Work Assignment No. 10

Project Officer

Robert W. Slater, Jr.
Physical Chemical Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/4-85/073		PB86 118585/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Validation of Soxhlet Extraction Procedure for SW-846	October 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Larry C. Michael, M. Arthur Moseley, John W. Hines Edo D. Pellizzari	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709	11. CONTRACT/GRANT NO. 68-03-3099
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Project Report 14. SPONSORING AGENCY CODE EPA/600/06

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The objective of this work assignment was to conduct a single-laboratory evaluation of the Soxhlet Extraction Procedure (Method 3540, SW-846) for the analysis of hazardous waste components in spent diatomaceous earth filter materials. The validation consisted of two phases: Phase 1, in which accuracy and precision were evaluated with diatomaceous earth fortified with a variety of analytes; and Phase 2, in which precision was determined by analysis of diatomaceous earth fortified with pesticide manufacturing waste. Several fortification/homogenization procedures were proposed and evaluated to accomplish Phase 1 objectives. The results show Method 3540 to be both accurate (average recovery: 90%) and precise (average percent relative standard deviation: 8%) on the recovery of nonvolatile analytes from diatomaceous earth.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	43
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-03-3099 to Research Triangle Institute. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as a USEPA document.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improve data collection, analysis, and quality control.

This report investigates the analytical behavior of selected organic pollutants in solid waste matrices. A suitable test procedure for their measurement is evaluated and data are presented to demonstrate the applicability of the method to a common chemical waste matrix.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

The objective of this work assignment was to conduct a single-laboratory evaluation of the Soxhlet Extraction Procedure (Method 3540, SW-846) for the analysis of hazardous waste components in spent diatomaceous earth filter materials. The validation consisted of two phases: Phase 1, in which accuracy and precision were evaluated with diatomaceous earth fortified with a variety of analytes; and Phase 2, in which precision was determined by analysis of diatomaceous earth fortified with pesticide manufacturing waste. Several fortification/homogenization procedures were proposed and evaluated to accomplish Phase 1 objectives. The results show Method 3540 to be both accurate (average recovery: 90%) and precise (average percent relative standard deviation: 8%) on the recovery of nonvolatile analytes from diatomaceous earth.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vi
Abbreviations and Symbols vii
Acknowledgment viii

1. Introduction 1
2. Conclusions and Recommendations 2
3. Materials and Methods 3
   Reagents and Standards 3
   Samples 3
   Methods 3
   Chromatographic Equipment 3
4. Experimental Procedures 5
   Gas Chromatography 5
   Development of Fortification/Homogenization Procedures 8
   Evaluation of Soxhlet Extraction Procedure with Fortified Reagent Filter Materials 9
   Evaluation of Soxhlet Extraction Procedure with Pesticide Manufacturing Waste 11
5. Results and Discussion 12
   Instrument Calibration 12
   Development of Fortification/Homogenization Procedures 12
   Evaluation with Fortified Reagent Filter Materials 19

Appendix

A. Soxhlet Extraction Procedure - Method 3540 (SW-846) 31

FIGURES

Number		Page
1	Capillary chromatogram of target analytes.....	6
2	Capillary chromatogram of Method Blank	18
3	Chromatogram of 100 percent recovery calibration.....	21
4	Chromatogram of extract of pesticide waste BML-10-07-04A....	23
5	Chromatogram of extract of pesticide waste BDB-6-19-01A.....	24
6	Chromatogram of extract of pesticide waste BDB-6-19-02A.....	25
7	Chromatogram of extract of pesticide waste R3236.....	26

TABLES

1	Pesticide Manufacturing Wastes Employed in Evaluation of Soxhlet Extraction Procedure.....	4
2	Retention of Analytes on SE-54 Capillary Column.....	7
3	Spiking Levels of Target Analytes.....	10
4	Linear Regression of Calibration Data.....	13
5	Quantitation of 100 Percent Recovery Standard Using the Calibration File.....	14
6	Comparison of Daily Calibrations with the Historical Calibration File.....	15
7	Summary of Matrix Fortification and System Recovery Experiments.....	17
8	Summary of Accuracy and Precision Data for Fortified Reagent Filter Media.....	20
9	Peak Assignments-Figure 3.....	22
10	Results of Analysis of Pesticide Waste BML-10-07-04A.....	27
11	Results of Analysis of Pesticide Waste BDB-6-19-01A.....	28
12	Results of Analysis of Pesticide Waste BDB-6-19-02A.....	29
13	Results of Analysis of Pesticide Waste R3236.....	30

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

SW-846	— Test Methods for Evaluating Solid Waste - Physical and Chemical Methods
RSD	— Relative standard deviation (standard deviation divided by the mean of observations)
K-D	— Kuderna-Danish evaporative concentrator
GC/FID	— Gas chromatograph with flame ionization detector
I.D.	— Internal diameter
2,4-D	— 2,4-Dichlorophenoxy acetic acid
MCPP	— 2-(4-Chloro-2-methylphenoxy) propionic acid
MCPA	— 2-(4-Chloro-2-methylphenoxy) acetic acid
p,p'-DDE	— 2,2-Bis(p-chlorophenyl)-1,1-dichloroethylene
p,p'-DDD	— 2,2-Bis(p-chlorophenyl)-1,1-dichloroethane
p,p'-DDT	— 1,1-Bis(p-chlorophenyl)-2,2,2-trichloroethane
I.S.	— Internal Standard
r	— Correlation coefficient

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of Dr. Mirtha Umana and Mr. Hu Burnett for their editorial review of the manuscript. The support of the Technical Project Monitor and staff at the U.S. Environmental Protection Agency - Office of Solid Waste in the acquisition of pesticide industry waste is also acknowledged.

SECTION 1

INTRODUCTION

Adsorption of waste materials on diatomaceous earth is a common practice of the chemical industry. In this process, a concentrated waste solution is filtered through a bed of diatomaceous earth to remove impurities. The resultant filter bed may contain relatively large amounts of organic compounds, up to 30 percent of the original filter weight, with individual components typically found at levels of 0.1 to 10 percent.

The Soxhlet Extraction Procedure (Method 3540, SW-846) was developed to provide the mechanism for monitoring hazardous waste constituents in diatomaceous earth filter materials. The primary objective of this Work Assignment was to provide validation of the Soxhlet Extraction Procedure (Method 3540) for the analysis of selected hazardous waste constituents in spent diatomaceous earth filter materials. This validation was designed to encompass analyte levels in the range of 0.1-10% (w/w) using both fortified reagent filter material and actual filter bed samples obtained from various pesticide manufacturing facilities.

The validation was conducted in two consecutive phases. Phase 1 involved development of procedures for fortification of reagent diatomaceous earth filter materials with 20 organic analytes representing various chemical classes. Accuracy and precision for the Soxhlet Extraction Procedure were assessed during this phase. In Phase 2, method precision was further verified by analysis of actual waste samples obtained from pesticide manufacturers.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The development and evaluation of fortification/homogenization procedures for preparing uniform distributions of analytes in diatomaceous earth showed no appreciable differences between fortification solvents, between mechanisms of homogenization, or between duration of homogenization. Uniformity of distribution of analytes in the diatomaceous earth was essentially independent of these parameters. Consequently, the most facile approach (i.e. fortifying using methylene chloride followed by tumbling for 30 min) was applied to subsequent experiments.

The evaluation of the Soxhlet Extraction Procedure (Method 3540, SW 846) using reagent diatomaceous earth demonstrated that this procedure provides accurate and precise measurements on nonvolatile components. Recoveries of such species from fortified diatomaceous earth were approximately 85 percent, with relative standard deviations of less than 11 percent. Recoveries of the three volatile analytes, toluene, p-xylene and o-xylene were considerably lower (~40%). Loss of these volatile compounds during evaporation of gross solvent in the fortification step was considered the most probable cause of this poor performance. Extraction and K-D evaporation were also minor contributors. No effect of using diatomaceous earth from different sources on recovery of target analytes was noted.

Precision of determination of unknown components of diatomaceous earth fortified with actual pesticide industry waste was somewhat lower (approximately 27% RSD). This observation was attributed to the difficulty of homogenizing a mixture of two solid materials.

Application of the extraction procedure to the analysis of actual diatomaceous earth filter materials (not "artificial" mixtures of diatomaceous earth and waste) would yield higher precision. The lack of such an application is an obvious limitation of this evaluation and it is recommended that it be included in subsequent studies.

SECTION 3
MATERIALS AND METHODS

REAGENTS AND STANDARDS

Compounds (reagent grade) required for matrix fortification were purchased from various commercial sources and were used as received. Reagent grade anhydrous sodium sulfate was purchased from Fisher Scientific Co. and was used as received. Two sources of diatomaceous earth were obtained, one from Johns-Manville and a second from J. T. Baker Chemical Co. Diatomaceous earth from both sources was purified, independently, by Soxhlet extraction with methylene chloride for 16 hr. Methylene chloride (Fisher, HPLC grade) was used without further purification.

SAMPLES

Samples of pesticide manufacturing waste were obtained from the Technical Project Monitor with assistance from the Office of Solid Waste (U.S. Environmental Protection Agency). These wastes are characterized in Table 1. Since no information was provided to the contrary, the samples were assumed not to be mixtures of diatomaceous earth and waste, but the actual waste itself. Consequently, they were mixed with preextracted diatomaceous earth to provide a surrogate filter waste containing 10% (w/w) waste. The homogenization procedure is discussed in detail in Section 4.

METHODS

All fortified diatomaceous earth samples, whether fortified with standard analytes or with actual waste, were extracted using the Soxhlet Extraction Procedure (Method 3540, SW-846). This entire procedure is presented in Appendix A. The basic components of the method are Soxhlet extraction with methylene chloride, drying through an anhydrous sodium sulfate column and solvent evaporation using a Kuderna-Danish (K-D) apparatus. Glassware was detergent washed, distilled water-rinsed, and heated to 260°C for 2 hr prior to each use.

CHROMATOGRAPHIC EQUIPMENT

Chromatograms were developed on a 50 m x 0.2 mm I.D. SE-54 fused silica capillary column (J&W Scientific Company) housed in a Varian 3700 gas chromatogram with a Grob-type injector and a flame ionization detector (GC/FID). Detector response was processed with a Nelson Analytical Model 4400 data system (based on a Hewlett-Packard 9826 computer). Chromatographic data were stored for subsequent reprocessing on 5-1/4 in. minifloppy disks.

TABLE 1. PESTICIDE MANUFACTURING WASTES EMPLOYED IN EVALUATION OF SOXHLET EXTRACTION PROCEDURE

Sample code	Composition provided	Physical description
BML-10-07-04A	50% (w/w) Methyl Parathion	sticky, heterogeneous solid mixture
BDB-6-19-01A	waste salts, ferrous chloride	dry, red-brown powder
BDB-6-19-02A	waste hexachlorobenzene	dry, sandy particles
R3236	organic liquid	two phase liquid (bottom methylene chloride miscible)

SECTION 4

EXPERIMENTAL PROCEDURES

GAS CHROMATOGRAPHY

Specific chromatographic conditions were determined for resolution of the analytes to be used in the evaluation. Figure 1 illustrates the separation attained using a 50 m x 0.2 mm I.D. SE-54 fused silica capillary column. Resultant retention times are shown in Table 2. A temperature program rate of three degrees per minute, with a 10-min initial temperature hold, was required to successfully separate the 21 analytes and three standards (n-decane, n-tetradecane, n-heneicosane). The chromatogram shows that 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP) and 2-(4-chloro-2-methylphenoxy) acetic acid (MCPA) peaks are barely visible above background at this level (1.2 µg/component injected; split 20:1). This is due to irreversible adsorption of these acids to the capillary column. Furthermore, this level is near the highest amount injected in this study. Consultations with research staff at J & W Scientific revealed that compounds of the acidity of 2,4-D, MCPP and MCPA cannot be successfully chromatographed underivatized on any known capillary column. Since derivatization was significantly outside of the scope of this Work Assignment, these three analytes were deleted from the target list prior to performing any evaluation experiments. Two alternate analytes, p-dichlorobenzene, and Methyl Parathion were added to the target list in lieu of these three acids.

The chromatographic system (Varian 3700 gas chromatograph with flame ionization detector; Nelson Analytical Model 4400 data system) was calibrated with 20 target analytes plus three internal standards. The chromatographic conditions are outlined in Table 2. Individual solutions of the 20 target analytes were prepared in either methylene chloride or methanol, depending upon solubility. Calibration standard mixtures of all analytes were prepared at 476, 238, and 95.2 ng/mL by combining aliquots of these individual solutions. These concentrations were selected to represent 100, 50, and 20 percent recovery of each analyte from diatomaceous earth under the conditions of the fortification/homogenization experiments. Standards were prepared in methylene chloride, with n-octane, n-tetradecane, and n-heneicosane added as internal standards at 2.00, 1.00, and 0.800 mg/mL, respectively, to the high-level calibration standard solution. The middle- and low-level solutions (corresponding to 50 and 20 percent recovery, respectively) were prepared by dilution of the high-level solution. Each calibration standard solution was analyzed in triplicate over a three-day time period. Slopes, y-intercepts, and correlation coefficients were computed by linear regression of the calibration data for each analyte and internal standard. A calibration file was created using the Nelson Analytical data system.

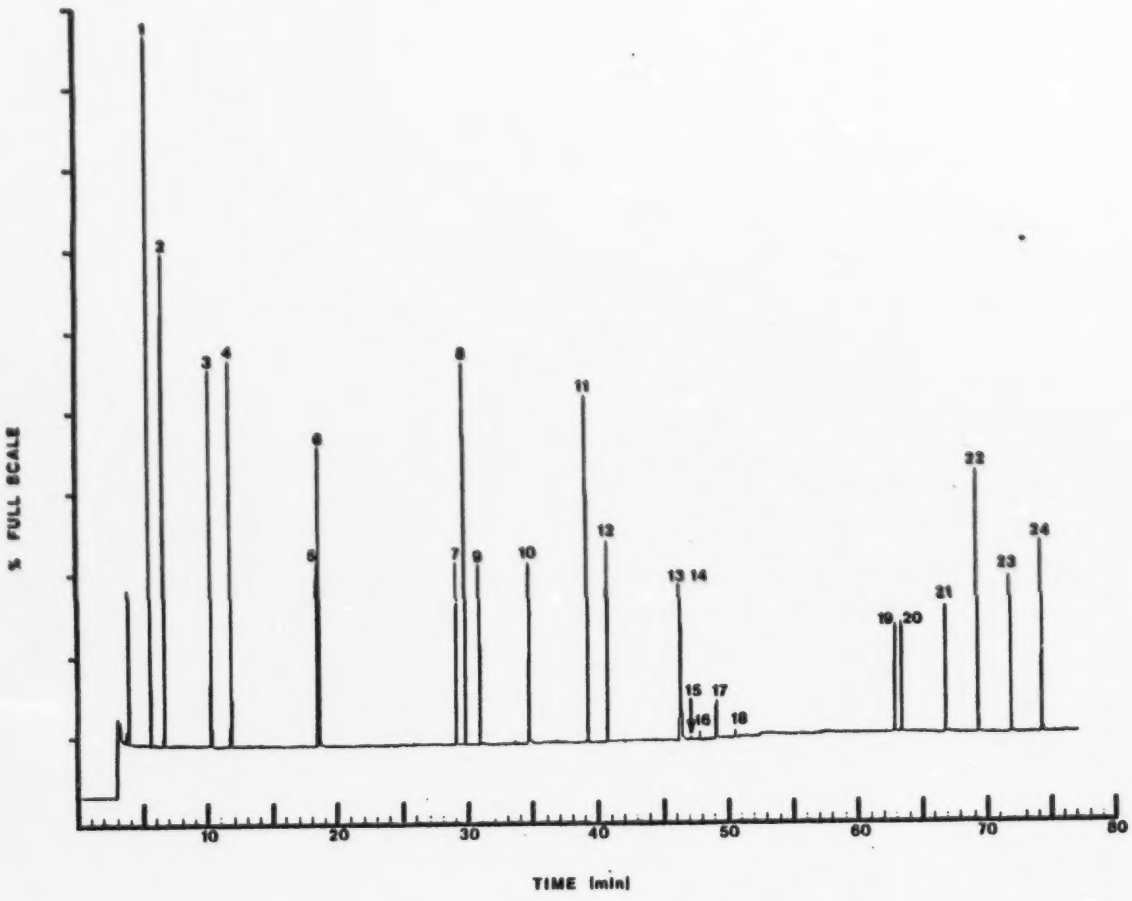

Figure 1. Capillary chromatogram of target analytes.
(see Table 2 for conditions)

TABLE 2. RETENTION OF ANALYTES ON SE-54 CAPILLARY COLUMN

Peak assignment	Compound	Retention time (min)[a]
1	toluene	5.6
2	n-decane (I.S. #1)	6.7
3	p-xylene	10.3
4	o-xylene	11.8
5	2-chlorophenol	18.5
6	phenol	18.8
b	p-dichlorobenzene[b]	19.9
7	2,4-dichlorophenol	29.1
8	naphthalene	29.8
9	2,6-dichlorophenol	30.9
10	4-chloro-o-cresol	34.7
11	2-chloronaphthalene	39.2
12	n-tetradecane (I.S. #2)	40.7
13	p-nitrophenol	46.3
14	2,4-dinitrotoluene	46.4
15	2,4-D	47.0
16	MCPP	47.8
17	p-nitroaniline	49.1
18	MCPA	50.6
b	Methyl Parathion[b]	60.0
19	Malathion	62.9
20	Parathion	63.4
21	n-heneicosane (I.S. #3)	66.9
22	p,p'-DDE	69.3
23	p,p'-DDD	72.0
24	p,p'-DDT	74.3

[a] 50 m x 0.2 mm I.D. SE-54 fused silica capillary column, 0.25 µm film thickness; temperature program: 40°C (10 min) to 260°C at 3°C/min; sweep time (He): 150 sec; 1.2 µg/component injected, split 20:1.

[b] Not shown on chromatogram (Figure 1).

DEVELOPMENT OF FORTIFICATION/HOMOGENIZATION PROCEDURES

The objective of the fortification experiments was to develop a procedure for spiking diatomaceous earth with the analytes that would produce a completely homogeneous matrix. The results of these experiments were evaluated primarily on the basis of reproducibility of recovery and not on the quantitativeness of recovery. Ultimately, the parameters to be evaluated include: (1) spiking solvent, (2) mixing procedure, and (3) mixing time. The diatomaceous earth used in the fortification/homogenization procedure development was obtained from Johns-Manville. Prior to performing the fortification/homogenization experiments, a method blank was prepared which consisted of 10 g of diatomaceous earth extracted with 300 mL of methylene chloride. The solvent extract volume was reduced to 10 mL using a Kuderna-Danish evaporative concentrator.

Four diatomaceous earth fortification experiments were performed at the 1% (total analyte mass) spiking level. In three of these experiments, spiked matrix was tumbled at 45 rotations/min using a motorized tumbling machine. The first and second fortification experiments utilized tumbling times of 0.5 and 24 hr, with methylene chloride as the spiking solvent. The third experiment also used a 0.5-hour tumbling time but differed in that methanol was used as the spiking solvent. The fourth experiment employed high-speed blending as a homogenization method.

The following analytical procedure was used in the fortification experiments. A clean, 16 oz, wide-mouth jar with a Teflon-lined cap was tared, and 35.00 g of precleaned diatomaceous earth was added. An aliquot (16.6 mL) of a solution (1. mg/mL) of each analyte was added and the combined weight obtained. This jar, which was one-third full of the spiked diatomaceous earth, was tumbled for the specified time. A preliminary experiment revealed that the methylene chloride solvent evaporated from the open jar at a rate of approximately 0.5 g/min. Therefore, gross methylene chloride was allowed to evaporate from the jar in a fume hood for 45 min in order to obtain a mixture that would maintain an approximately constant mass during the weighing process. During this evaporation, the jar was capped every 10 min and shaken manually for 1 min to rehomogenize the sample. Triplicate aliquots (approximately 10 g) of the spiked matrix were withdrawn from the jar, added to tared cellulose extraction thimbles, and the weight of the thimble and diatomaceous earth recorded. Method 3540 of SW-846 was followed precisely for the Soxhlet extraction and solvent reduction procedures. Internal standards were added to the concentrated extract immediately following the K-D step but prior to transfer of the extract to a storage vial. Concentrated extracts were analyzed by capillary GC/FID.

Prior to performing the third fortification experiment, an aliquot of the standard solution of analytes in methylene chloride was solvent-exchanged to an equivalent volume of methanol using a K-D apparatus. The resultant methanolic solution was used for spiking the diatomaceous earth as well as to prepare a new calibration standard. This standard was analyzed on the same day as the diatomaceous earth extracts. The amount of each analyte spiked was calculated from the results of the analysis of this standard. This was done to correct the amount spiked for any losses of analytes which occurred during solvent exchange.

The utility of high-speed blending relative to low-speed tumbling as a homogenization method was investigated. This fortification experiment utilized methylene chloride as the spiking solvent with analytes spiked at the 1% w/w (total weight of all analytes) level. The blender container, constructed of stainless steel and Teflon, was cleaned prior to use by solvent-rinsing with methylene chloride, methanol, and toluene and subsequently dried with a stream of nitrogen gas. Diatomaceous earth (35.15 g) was added to the tared container and spiked with 16.6 mL of a 1.0 mg/mL solution of all of the analytes in methylene chloride. The container was reweighed, and the blender turned on to medium setting for 30 sec. A visual inspection of the contents revealed that the blades had cut a cavern and were not significantly mixing the earth. Therefore, the mixture was stirred with a glass rod, after which the blender was turned on for an additional 30 sec. This cycle was repeated a total of three times. The top of the container was then removed and the mixture allowed to air dry for 45 min, with manual stirring every 10 min to permit uniform drying. At the end of this drying period, the container and contents were reweighed, revealing a loss of 9.15 g of methylene chloride by evaporation. The spiked diatomaceous earth was aliquoted into three cellulose extraction thimbles which were subsequently processed by Method 3540.

To determine the recovery of the target analytes through the analytical procedure, an experiment was carried out which excluded diatomaceous earth during the Soxhlet Extraction Procedure. Triplicate cellulose extractor thimbles were loaded with 10 g of sodium sulfate and a glass wool plug. Target compounds (5 mL of a 1.0 mg/mL solution) were spiked directly onto the sodium sulfate and the extraction executed according to Method 3540.

EVALUATION OF SOXHLET EXTRACTION PROCEDURE WITH FORTIFIED REAGENT FILTER MATERIALS

Diatomaceous earth was fortified and homogenized by the procedure described in detail in Section 4. Fortified diatomaceous earth was analyzed in five replicates plus a single unfortified aliquot (i.e., blank). Precleaned diatomaceous earth (50.0 g) was added to a clean 16 oz wide-mouth jar. The stock solution of target analytes was added in volumes necessary to produce the spiking levels specified (Table 3). Volumes required for the high, middle, and low spiking levels were 352 mL, 176 mL and 35.2 mL, respectively. The methylene chloride solvent for the stock solution was allowed to evaporate from the jar in a fume hood to obtain a powdery mixture which would not stick to the walls of the jar while tumbling. During this evaporation, the mixture was stirred every 30 min to homogenize the sample. After evaporation of gross solvent, the jar was capped, and tumbled for 30 min at approximately 45 rotations/minute. Aliquots of the spiked diatomaceous earth were added to tared cellulose extraction thimbles which were subsequently reweighed to determine the exact weight aliquoted. Method 3540 of the SW-846 manual was followed precisely for the Soxhlet extraction and solvent reduction procedures. Internal standards were added to the concentrated extract immediately following the K-D step but prior to transfer of the extract to a storage vial. Concentrated extracts were stored at 4°C until analyzed by capillary GC/FID.

TABLE 3. SPIKING LEVELS OF TARGET ANALYTES

Analyte	Fortification levels(%)		
Malathion	10	5	1
Parathion	1	0.5	0.1
p,p'-DDD	1	0.5	0.1
p,p'-DDE	1	0.5	0.1
p,p'-DDT	1	0.5	0.1
p-nitrophenol	1	0.5	0.1
p-nitroaniline	1	0.5	0.1
2,4-dinitrotoluene	1	0.5	0.1
2-chlorophenol	1	0.5	0.1
phenol	10	5	1
4-chloro-o-cresol	1	0.5	0.1
2,4-dichlorophenol	1	0.5	0.1
2,6-dichlorophenol	1	0.5	0.1
toluene	1	0.5	0.1
o-xylene	10	5	1
p-xylene	1	0.5	0.1
naphthalene	1	0.5	0.1
2-chloronaphthalene	1	0.5	0.1
Methyl Parathion	10	5	1
p-dichlorobenzene	10	5	1
Total % Loaded	65	32.5	6.5
g Analyte/10 g Matrix	6.5	3.25	0.65

EVALUATION OF SOXHLET EXTRACTION PROCEDURE WITH PESTICIDE MANUFACTURING WASTE

The industrial samples employed in this evaluation were not diatomaceous earth filter samples. Therefore, these samples were incorporated into precleaned diatomaceous earth at a 10% w/w level using the same method which had been applied to the fortification of clean filter material with target analytes. Pesticide manufacturing waste (7 g) was added to 70 g of precleaned diatomaceous earth in a 16 oz ointment jar and the mixture tumbled for 30 min at 45 rotations/minute. Aliquots (10 g) were dispensed to tared cellulose extraction thimbles and extracted by Method 3540.

SECTION 5

RESULTS AND DISCUSSION

INSTRUMENT CALIBRATION

Slopes, y-intercepts and correlation coefficients for the linear regression of the calibration data are summarized in Table 4. In all cases, the correlation coefficients exceeded 0.99, indicating that the calibration line is quite linear. Percent relative standard deviations for the replicate analysis of each of the three standard solutions averaged near 10 percent.

Results from the Nelson Analytical calibration file used to reanalyze the three calibration solutions are shown in Table 5. Relative standard deviations are less than 5 percent in most cases for triplicate analysis. Deviations between the calculated and measured concentrations, expressed as percent bias, are also less than 5 percent with the exception of p-nitroaniline and p,p'-DDD, which are appreciably higher. Since these high values are found in all the standard files, a poor calibration for these two compounds is suspected.

The above results dictate that the acceptable range into which the daily calibration standard must fall is +/-10 percent, with the exception of phenol and p-nitroaniline, where this range is twice the standard deviation. Results of the analyses of the daily calibration standards and the acceptable ranges are presented in Table 6.

DEVELOPMENT OF FORTIFICATION/HOMOGENIZATION PROCEDURES

The results of the fortification experiments are summarized in Table 7. System recovery data are also shown in Table 7 for comparison. These values represent optimum recovery and precision since no diatomaceous earth was present during extraction. In all cases, the mean percent relative standard deviation was less than 13. If values for toluene, p-xylene, and o-xylene are excluded, the mean % RSD's do not exceed 8. This lack of precision observed for toluene, p-xylene, and o-xylene is undoubtedly attributable to losses of these analytes during evaporation of solvent in the fortification step and not to a nonhomogeneous distribution in the matrix. Lack of uniform distribution by any homogenization procedure is, in fact, refuted by the other analytes which show nearly quantitative recoveries and excellent precision for replicate samples. A chromatogram of the method blank, illustrated in Figure 2, reveals no interferences at the lowest fortification level.

Comparison of the % RSD's for the four fortification/homogenization experiments with those of the system recovery shows only slight differences.

TABLE 4. LINEAR REGRESSION OF CALIBRATION DATA

	Slope	Y-Int.	r[a]
toluene	44.4	69	0.998
n-octane(I.S.#1)	45.7	47	0.999
p-xylene	45.1	-9	0.999
o-xylene	45.0	40	0.999
2-chlorophenol	23.2	36	0.999
phenol	33.2	-61	0.999
p-dichlorobenzene	22.5	-183	0.996
2,4-dichlorophenol	18.5	2	0.999
naphthalene	44.6	270	0.999
2,6-dichlorophenol	18.4	43	0.999
4-chloro-o-cresol	23.7	132	0.999
2-chloronaphthalene	35.3	336	0.999
n-tetradecane(I.S.#2)	23.1	193	0.999
p-nitrophenol	18.4	74	0.999
2,4-dinitrotoluene	16.5	-288	0.998
p-nitroaniline	13.9	606	0.994
Methyl Parathion	9.66	-238	0.995
Malathion	7.79	310	0.994
Parathion	11.5	365	0.996
n-heneicosane(I.S.#3)	15.5	641	0.994
p,p'-DDE	18.7	779	0.996
p,p'-DDD	17.0	620	0.997
p,p'-DDT	16.2	625	0.998

[a]Correlation coefficient

TABLE 5. QUANTITATION OF 100 PERCENT RECOVERY STANDARD USING THE CALIBRATION FILE

Compound	Concentration (µg/µL) Calculated	Determined	(% RSD)[a]	% Bias[b]
toluene	1.00	1.00	(0.15)	0
p-xylene	1.00	1.00	(0.68)	0
o-xylene	10.0	10.0	(0.12)	0
2-chlorophenol	1.00	1.02	(2.9)	2.0
phenol	10.0	9.4	(13)	-6.0
p-dichlorobenzene	10.0	9.9	(2.9)	-1.0
2,4-dichlorophenol	1.00	1.02	(3.3)	2.0
naphthalene	1.00	1.00	(2.8)	0
2,6-dichlorophenol	1.00	1.01	(2.5)	1.0
4-chloro-o-cresol	1.00	1.02	(2.3)	2.0
2-chloronaphthalene	1.00	0.99	(1.9)	-1.0
p-nitrophenol	1.00	1.01	(2.6)	1.0
2,4-dinitrotoluene	1.00	1.05	(9.2)	5.0
p-nitroaniline	1.00	1.18	(14)	18
Methyl Parathion	10.0	10.2	(2.0)	2.0
Malathion	10.0	9.9	(4.0)	-1.0
Parathion	1.00	0.97	(8.4)	-3.0
p,p'-DDE	1.00	1.01	(2.3)	1.0
p,p'-DDD	1.00	1.20	(9.6)	20
p,p'-DDT	1.00	0.97	(7.3)	-3.0

[a]Triplicate determinations.

[b] $\% \text{ Bias} = \frac{1}{N} \sum \frac{X_i - X_a}{X_a} \cdot 100$; where X_a = accepted value.

TABLE 6. COMPARISON OF DAILY CALIBRATIONS WITH THE HISTORICAL CALIBRATION FILE

Analyte	Acceptable Range[a]			Daily Calibrations									
	Mean[b]	Max[c]	Min[c]	1	2	3	4	5	6	7	8	9	10
toluene	0.99	1.09	0.89	1.03	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.04	1.01
p-xylene	1.00	1.10	0.90	1.04	1.00	1.00	1.00	1.00	1.01	1.00	1.04	1.00	1.02
o-xylene	9.99	11.0	8.99	1.04	10.0	10.0	10.0	10.0	10.1	10.0	10.1	9.96	10.2
2-chlorophenol	1.02	1.12	0.92	1.06	1.05	1.03	1.04	1.04	1.04	1.05	1.04	1.05	1.06
phenol	9.44	10.7[d]	8.22[d]	10.4	10.4	10.2	10.1	10.2	10.2	10.2	10.2	10.1	10.3
p-dichlorobenzene	9.94	10.9	8.95	10.1	10.3	10.2	9.86	10.1	10.2	9.93	10.2	10.0	10.5
2,4-dichlorophenol	1.02	1.10	0.92	1.02	1.06	1.04	1.03	1.05	1.07	1.03	1.05	1.04	1.09
naphthalene	1.00	1.09	0.90	1.01	1.03	1.02	0.98	1.02	1.03	1.00	1.02	1.01	1.04
2,6-dichlorophenol	1.01	1.11	0.91	1.03	1.07	1.02	1.02	1.06	1.07	1.04	1.05	1.05	1.08
4-chloro-o-cresol	1.02	1.12	0.92	1.02	1.07	1.01	1.02	1.05	1.06	1.05	1.04	1.04	1.08
2-chloronaphthalene	1.00	1.10	0.90	1.03	1.02	1.01	1.00	1.03	1.05	1.03	1.03	1.01	1.05
p-nitrophenol	1.01	1.11	0.91	1.08	0.99	0.96	0.95	0.93	0.97	0.95	0.93	0.96	0.95
2,4-dinitrotoluene	1.05	1.16	0.94	1.11	1.09	1.03	1.11	1.17	1.18[e]	1.12	1.17[e]	1.12	1.17
p-nitroaniline	1.18	1.35[d]	1.01[d]	0.77[e]	1.18	1.25	1.27	1.24	0.87[c]	1.35	0.76[e]	1.29	1.30
Methyl Parathion	10.2	11.2	9.18	10.5	9.83	6.48[f]	10.4	10.5	10.5	10.5	10.3	9.96	10.2
Malathion	9.89	10.9	8.90	10.4	9.04	10.3	10.3	9.83	10.3	10.6	10.3	9.83	10.2
Parathion	0.97	1.06	0.87	1.05	0.87[f]	1.03	1.02	0.96	1.00	0.97	1.00	0.95	0.98
p,p'-DDE	1.01	1.11	0.91	1.08	0.96	1.05	1.06	1.02	1.08	1.08	1.08	1.02	1.04
p,p'-DDD	1.20	1.32	1.08	1.35[f]	1.16	1.26	1.32	1.23	1.41[f]	1.34[f]	1.34[f]	1.27	1.29
p,p'-DDT	0.97	1.07	0.88	1.08	0.93	1.01	1.07	1.00	1.14[f]	1.08	1.08	1.03	1.05

TABLE 6. (Continued)

Analyte	Acceptable Range[a]			Daily Calibrations								
	Mean[b]	Max[c]	Min[c]	11	12	13	14	15	16	17	18	19
toluene	0.99	1.09	0.89	1.01	0.99	1.00	0.99	1.00	1.00	1.01	1.00	1.01
p-xylene	1.00	1.10	0.90	1.02	1.00	1.00	0.99	1.02	1.00	1.02	1.01	1.02
o-xylene	9.99	11.0	8.99	10.2	10.0	10.0	9.98	10.2	10.0	10.1	10.1	10.2
2-chlorophenol	1.02	1.12	0.92	1.07	1.06	1.05	1.03	1.06	1.04	1.05	1.05	1.07
phenol	9.44	10.7[d]	8.22[d]	10.2	10.3	10.1	9.99	10.2	10.3	10.0	10.3	10.4
p-dichlorobenzene	9.94	10.9	8.95	10.2	9.60	9.99	10.0	10.5	10.1	10.6	10.2	10.2
2,4-dichlorophenol	1.02	1.10	0.92	1.06	1.02	1.05	1.04	1.04	1.05	1.05	1.06	1.04
naphthalene	1.00	1.09	0.90	1.02	0.98	1.00	0.98	1.01	1.01	1.03	1.02	1.02
2,6-dichlorophenol	1.01	1.11	0.91	1.08	1.02	1.03	1.02	1.02	1.04	1.05	1.06	1.06
4-chloro-o-cresol	1.02	1.12	0.92	1.07	1.04	1.03	1.01	0.99	1.03	1.01	1.05	1.04
2-chloronaphthalene	1.00	1.10	0.90	1.03	1.02	1.01	0.99	0.98	1.01	0.99	1.03	1.02
p-nitrophenol	1.01	1.11	0.91	1.01	0.99	0.98	0.95	0.87[e]	0.97	0.94	1.05	1.04
2,4-dinitrotoluene	1.05	1.16	0.94	1.20	1.16	1.16	1.11	0.99	1.10	0.99	1.17[e]	1.13
p-nitroaniline	1.18	1.35[d]	1.01[d]	1.27	1.26	1.36[e]	1.17	1.04	1.24	1.15	1.30	1.26
Methyl Parathion	10.2	11.2	9.18	10.2	8.62[f]	10.1	9.93	9.82	9.96	9.78	10.6	10.3
Malathion	9.89	10.9	8.90	10.2	9.03	9.52	10.2	9.63	9.94	9.77	10.3	10.0
Parathion	0.97	1.06	0.87	0.93	0.87[f]	0.88	0.90	0.87[f]	0.96	0.94	0.99	0.97
p,p'-DDE	1.01	1.11	0.91	1.05	0.93	1.00	1.04	1.01	1.03	1.02	1.07	1.04
p,p'-DDD	1.20	1.32	1.08	1.27	1.06	1.07	1.14	1.14	1.22	1.16	1.17	1.20
p,p'-DDT	0.97	1.07	0.88	1.03	0.89	0.90	0.95	0.96	1.03	1.00	1.01	1.00

[a] Concentrations in µg/mL.

[b] Three determinations.

[c] Minimum = Mean - 10%; Maximum = Mean + 10%.

[d] Minimum = Mean - 2(S.D.); Maximum = Mean + 2(S.D.).

[e] Compound out-of-range - poor chromatographic resolution.

[f] Compound out-of-range.

TABLE 7. SUMMARY OF MATRIX FORTIFICATION AND SYSTEM RECOVERY EXPERIMENTS

Compound	% Recovery (% RSD)[a] Fortification experiment 1[b]	Fortification experiment 2[c]	Fortification experiment 3[d]	Fortification experiment 4[e]	System recovery[f]
toluene	9.02 (73.7)	1.09 (118)	— [g]	1.75 (31.5)	70.5 (3.52)
p-xylene	31.0 (44.6)	12.6 (45.1)	50.3 (13.4)	44.4 (16.0)	90.1 (1.48)
o-xylene	37.6 (37.4)	18.1 (36.2)	48.4 (6.88)	51.9 (13.7)	92.5 (1.32)
phenol	92.3 (5.10)	83.1 (2.89)	92.2 (2.36)	103 (9.80)	100 (0.808)
2-chlorophenol	97.7 (4.89)	89.9 (0.642)	95.9 (2.89)	106 (3.77)	100 (0.757)
p-dichlorobenzene	—[g]	—	—	—	—
2,4-dichlorophenol	107 (2.36)	99.3 (0.895)	99.1 (3.04)	111 (9.46)	105 (2.75)
naphthalene	99.6 (1.22)	88.2 (1.37)	89.4 (2.10)	106 (5.37)	104 (1.47)
2,6-dichlorophenol	109 (1.92)	100 (0.721)	97.7 (3.84)	113 (4.93)	106 (1.96)
4-chloro-o-cresol	107 (3.37)	102 (1.14)	98.6 (4.28)	112 (4.97)	102 (2.91)
2-chloronaphthalene	107 (3.24)	99.3 (1.50)	95.3 (3.69)	111 (5.43)	104 (2.42)
p-nitrophenol	105 (8.89)	98.9 (4.14)	102 (9.03)	108 (2.97)	96.9 (2.37)
2,4-dinitrotoluene	107 (7.16)	97.5 (3.14)	100 (10.0)	109 (6.88)	97.3 (4.32)
p-nitroaniline	132 (7.34)	122 (4.95)	213 (11.3)	135 (3.39)	116 (3.02)
Methyl Parathion	—[g]	—	—	—	—
Malathion	121 (0.952)	114 (2.54)	104 (5.74)	118 (7.87)	109 (3.22)
Parathion	121 (1.91)	111 (1.38)	103 (6.06)	114 (5.47)	105 (2.91)
p,p'-DDE	121 (0.952)	114 (2.32)	102 (5.19)	121 (6.42)	112 (2.90)
p,p'-DDD	121 (0.826)	116 (1.72)	101 (7.57)	122 (6.35)	112 (3.71)
p,p'-DDT	122 (1.26)	117 (1.78)	101 (8.46)	123 (6.77)	112 (4.09)
Mean recovery	97.1	88.0	99.6	101	102
Mean % RSD	11.5	12.8	6.22	8.39	2.55
Mean % RSD[h]	7.85	6.61	6.22	7.03	2.49

[a] Mean of triplicate determinations; percent relative standard deviation.
[b] Target compounds spiked in methylene chloride; matrix homogenized by tumbling for 0.5 hr.
[c] Target compounds spiked in methylene chloride; matrix homogenized by tumbling for 24 hr.
[d] Target compounds spiked in methanol; matrix homogenized by tumbling for 0.5 hr.
[e] Target compounds spiked in methylene chloride; matrix homogenized by blending for 0.5 hr.
[f] No diatomaceous earth present.
[g] No data.
[h] Excluding toluene.

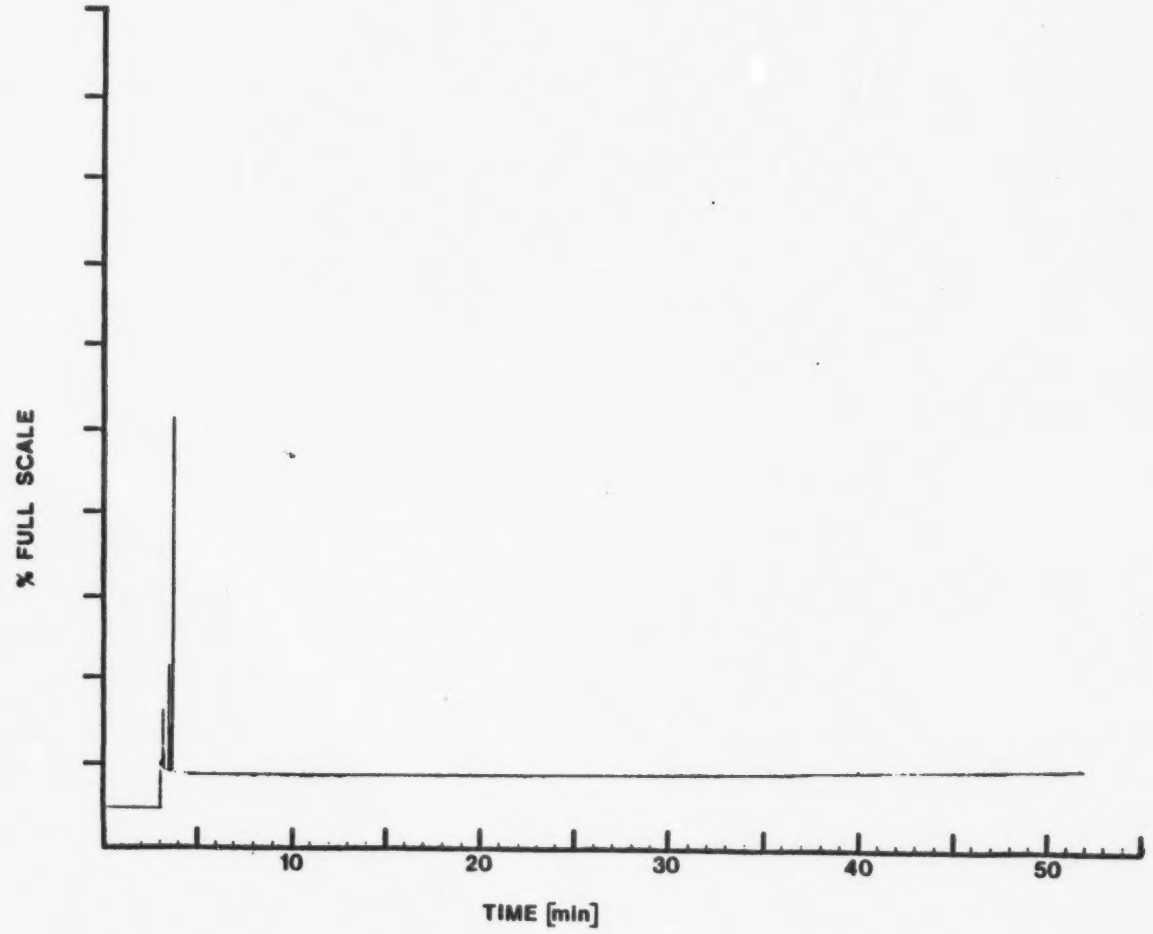

Figure 2. Capillary chromatogram of Method Blank. 50 m x 0.2 mm I.D. SE-54 fused silica capillary column; temperature program: 40° C to 260° C at 3° C/min; sweep time (He): 150 sec; 1.5 µL injection, split 20:1.

The mean percent relative standard deviation for the system recovery is approximately 40 percent of those of the fortification experiments, indicating that there is a small but significant irreproducibility associated with the matrix homogenizing/aliquoting process. Differences in precision between the four fortification experiments are insignificant, particularly if the data for toluene are excluded. Matrix fortification with methylene chloride followed by mechanical tumbling for 30 min is the most facile procedure and was therefore chosen for use in subsequent evaluations.

EVALUATION WITH FORTIFIED REAGENT FILTER MATERIALS

The results of the fortification experiments are summarized in Table 8. Accuracy is expressed as percent recovery, where recovery has been calculated as the ratio of the amount of a given analyte detected to the amount added to the sample prior to extraction. The amount of analyte detected is computed from the chromatographic detector response relative to the response to a standard solution. Precision is expressed as percent relative standard deviation.

As noted previously in the results of the fortification/homogenization experiments, there are distinctly lower recoveries for toluene, p-xylene and o-xylene. These analytes are strongly suspected of being lost during solvent evaporation. Generally, the recoveries of all other targets (Table 8) are very high and very precise. The mean recovery for all analytes in all samples is 83.6. Similarly, the mean percent relative standard deviation is 7.5. Neither percent recovery nor percent relative standard deviation shows any dependence on fortification level or diatomaceous earth source. No effect of analyte type on either accuracy or precision is noted.

Figure 3 illustrates a representative chromatogram of the standard solution used for analyte quantitation. Peak assignments for this chromatogram are presented in Table 9. Chromatograms of waste sample extracts are shown in Figures 4 through 7. Results of these analyses (Tables 10 through 13) have been expressed either as mg analyte/g waste, where specific peak identifications were possible, or as normalized area ratios where sample component identities could not be made. Normalized area ratios were computed as the ratio of the peak area of the compound of interest to the peak area of the nearest eluting internal standard, all divided by the mass of pesticide waste extracted.

The precision (% RSD) of the analysis of the six replicate samples ranged from 10 to 46, with a mean of 27, and is significantly poorer than that associated with analysis of analyte-fortified diatomaceous earth samples (mean % RSD = 7.5). This is most likely the result of nonhomogeneity of the pesticide waste-diatomaceous earth mixture used to mimick actual waste filter media. Although this waste mixture was homogenized using the same procedure as was used for the analyte-fortified samples, in most cases the waste sample was a solid and was, therefore, not as readily distributed throughout the diatomaceous earth. This is confirmed by the single liquid sample, R3236, which demonstrated a mean precision of 10 percent.

TABLE 8. SUMMARY OF ACCURACY AND PRECISION DATA[a] FOR FORTIFIED REAGENT FILTER MEDIA

	Fort. Level 1[b]				Fort. Level 2[c]				Fort. Level 3[d]			
	DE1[e]		DE2[f]		DE1		DE2		DE1		DE2	
Analyte	Rec(%)[g]	RSD(%)[h]	Rec(%)	RSD(%)	Rec(%)	RSD(%)	Rec(%)	RSD(%)	Rec(%)	RSD(%)	Rec(%)	RSD(%)
toluene	28.4	10.3	18.5	9.3	24.5	6.9	30.5	11	11.5	60	47.9	9.7
p-xylene	49.2	2.2	31.3	22	43.2	5.4	49.9	5.8	30.8	38	67.4	8.8
o-xylene	54.5	2.3	39.3	4.3	48.2	5.2	54.9	5.4	36.9	32	70.8	9.0
2-chlorophenol	82.0	3.2	76.5	8.5	83.1	4.2	84.5	3.7	77.3	7.4	87.3	11
phenol	83.5	3.0	80.5	10	86.3	4.3	86.6	3.0	77.8	12	86.4	11
p-dichlorobenzene	74.2	1.6	61.6	3.2	66.1	8.1	70.2	3.9	58.5	14	78.7	11
2,4-dichlorophenol	92.0	2.5	87.3	5.5	94.9	5.0	92.0	3.0	90.9	2.4	89.5	12
naphthalene	87.2	1.9	80.7	5.0	86.2	4.7	84.8	3.2	82.0	1.7	85.3	12
2,6-dichlorophenol	92.3	2.0	88.1	6.1	95.2	4.7	93.3	3.5	91.3	1.9	89.4	12
4-chloro-o-cresol	92.8	1.3	90.4	6.6	97.1	5.2	93.5	2.7	90.8	2.1	88.5	12
2-chloronaphthalene	90.9	1.9	87.1	6.1	93.4	4.9	89.5	1.9	90.5	2.5	87.5	12
p-nitrophenol	86.2	2.8	83.5	7.7	93.8	5.6	86.3	5.5	91.6	4.4	84.9	8.4
2,4-dinitrotoluene	101	2.1	98.0	8.1	105	4.3	95.4	7.1	99.1	5.4	96.5	7.7
p-nitroaniline	115	3.1	112	6.2	122	7.0	99.6	19	119	4.8	112	9.1
Methyl Parathion	92.2	3.5	87.3	6.9	90.9	12.4	93.7	3.8	97.3	3.5	91.6	11
Malathion	89.6	4.1	85.5	6.3	89.0	10.3	92.0	3.1	96.2	3.2	92.2	9.1
Parathion	87.2	6.8	79.6	8.4	84.4	11.1	91.5	5.9	93.9	3.8	89.4	8.9
p,p'-DDE	94.0	3.4	89.6	6.4	92.8	10.8	92.5	3.4	98.6	4.1	94.6	9.2
p,p'-DDD	114	6.3	112	7.0	110	15.1	108	7.6	124	5.2	118	8.5
p,p'-DDT	93.6	6.7	89.9	8.6	89.8	12.4	95.7	1.8	99.5	4.7	97.1	10
Mean	85.0	3.6	78.9	7.6	84.8	7.4	82.2	5.2	82.9	11	87.7	10

[a] Based on 5 replicates.
[b] Fortification Level 1 (see Table 3-9).
[c] Fortification Level 2 (see Table 3-9).
[d] Fortification Level 3 (see Table 3-9).
[e] Diatomaceous earth #1, Johns Manville.
[f] Diatomaceous earth #2, J. T. Baker.
[g] Percent recovery.
[h] Percent relative standard deviation.

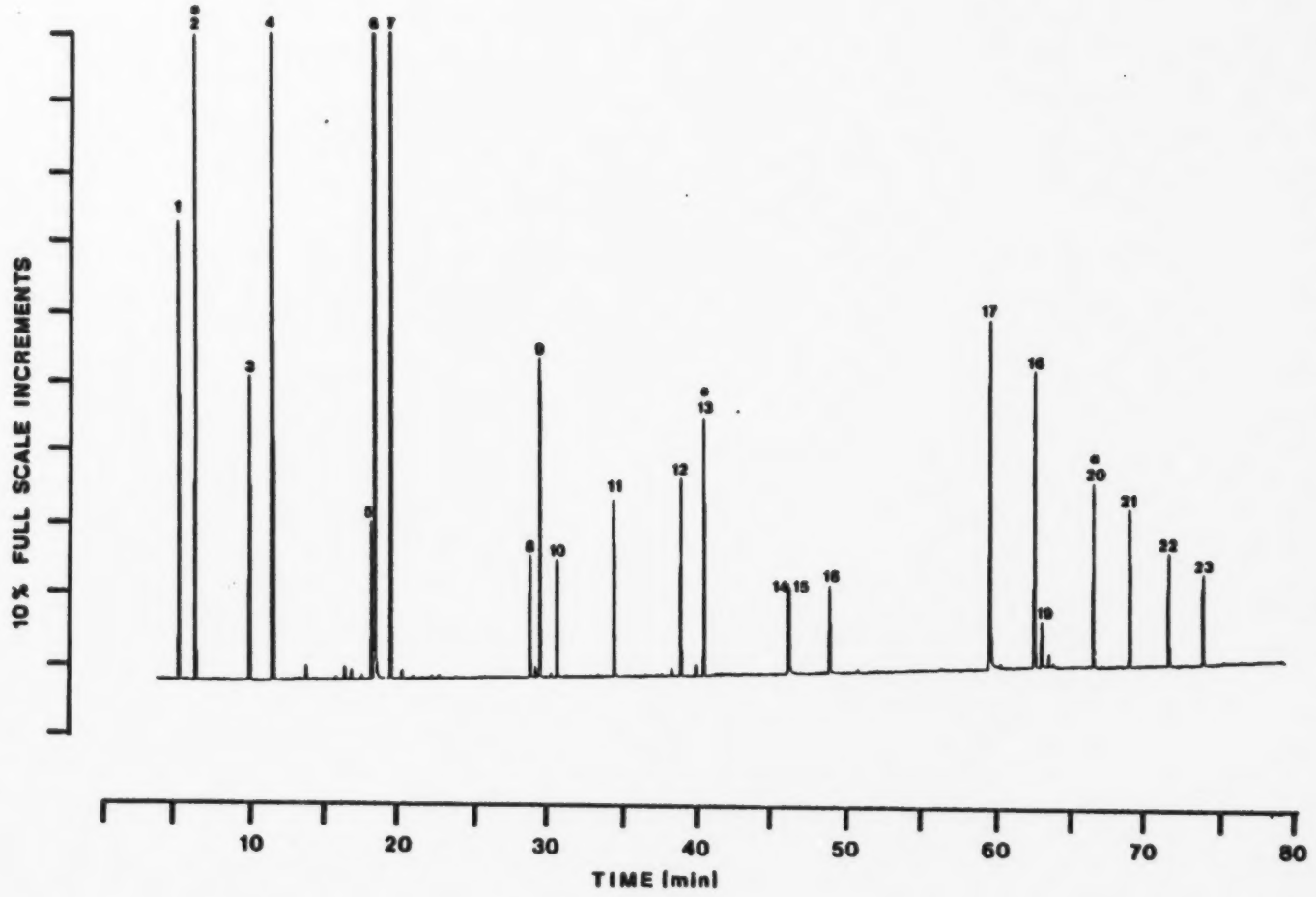

Figure 3. Chromatogram of 100 percent recovery calibration standard (see Table 2 for conditions); asterisk denotes internal standard.

TABLE 9. PEAK ASSIGNMENTS-FIGURE 3.

Peak Number	Analyte
1	toluene
2	n-octane (I.S.#1)
3	p-xylene
4	o-xylene
5	2-chlorophenol
6	phenol
7	p-dichlorobenzene
8	2,4-dichlorophenol
9	naphthalene
10	2,6-dichlorophenol
11	4-chloro-o-cresol
12	2-chloronaphthalene
13	n-tetradecane (I.S.#2)
14	p-nitrophenol
15	2,4-dinitrotoluene
16	p-nitroaniline
17	Methyl Parathion
18	Malathion
19	Parathion
20	n-heneicosane (I.S.#3)
21	p,p'-DDE
22	p,p'-DDD
23	p,p'-DDT

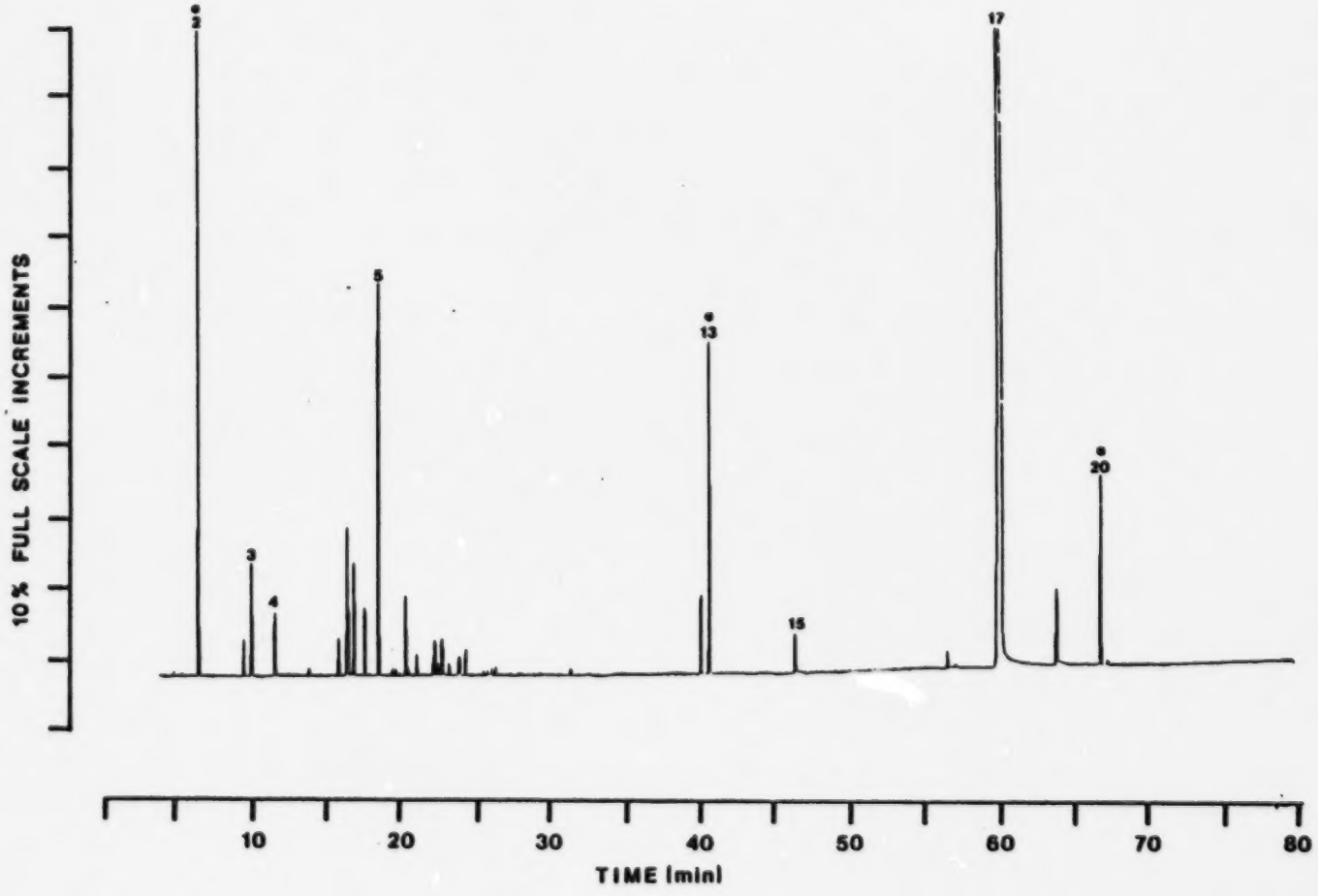

Figure 4. Chromatogram of extract of pesticide waste BML-10-07-04A (see Table 2 for conditions); asterisk denotes internal standard.

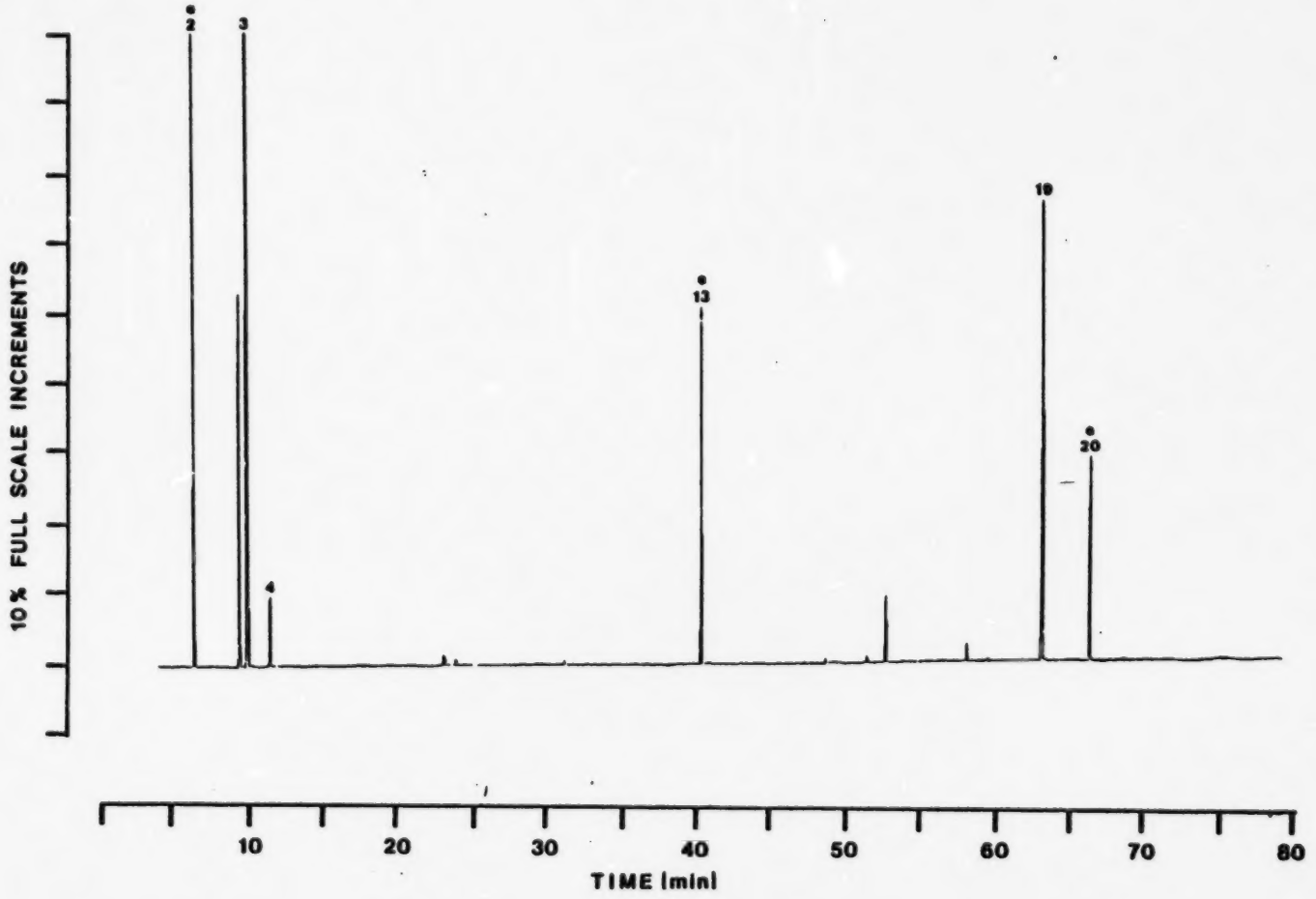

Figure 5. Chromatogram of extract of pesticide waste BDB-6-19-01A (see Table 2 for conditions); asterisk denotes internal standard.

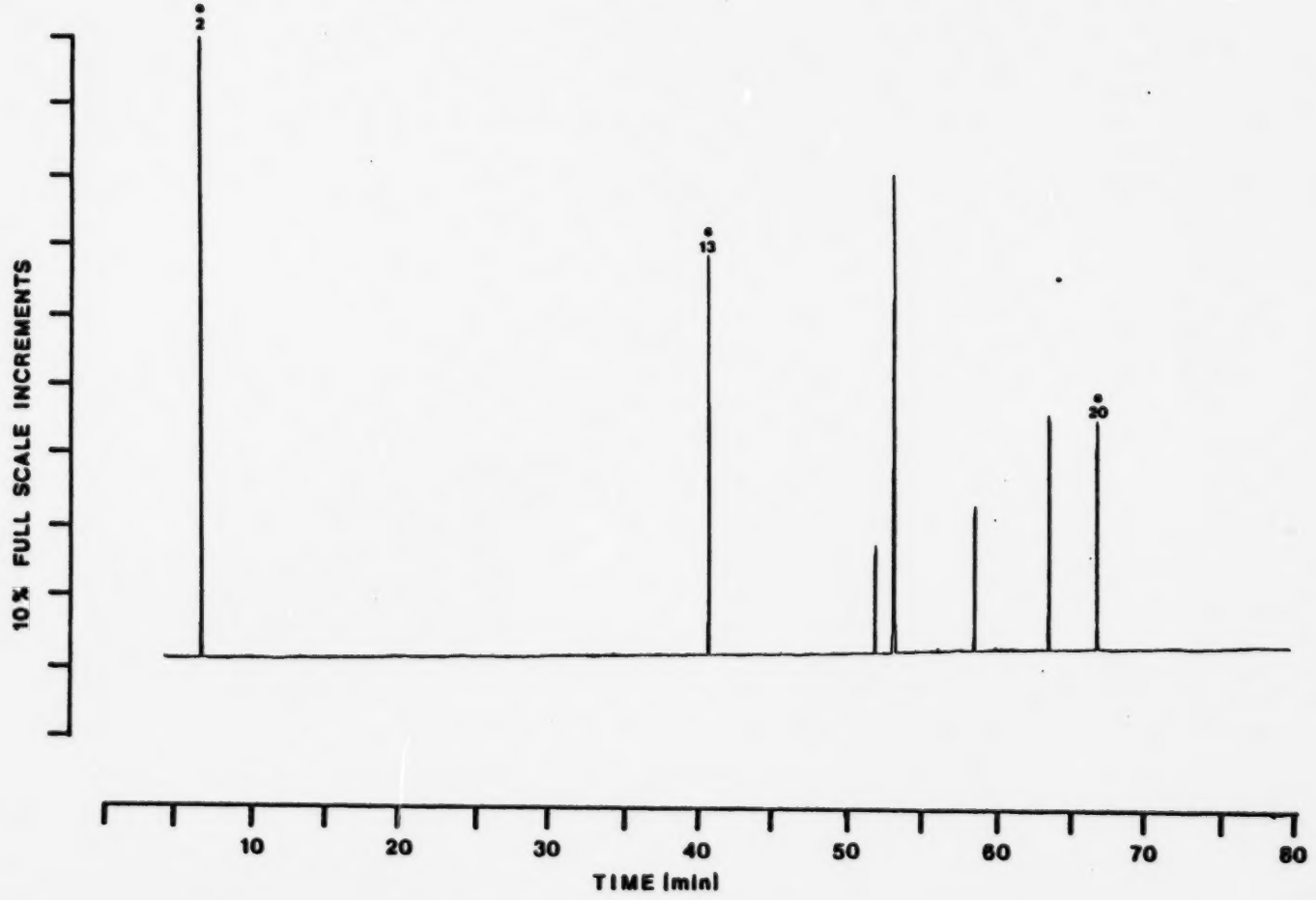

Figure 6. Chromatogram of extract of pesticide waste BDB-6-19-02A (see Table 2 for conditions); asterisk denotes internal standard.

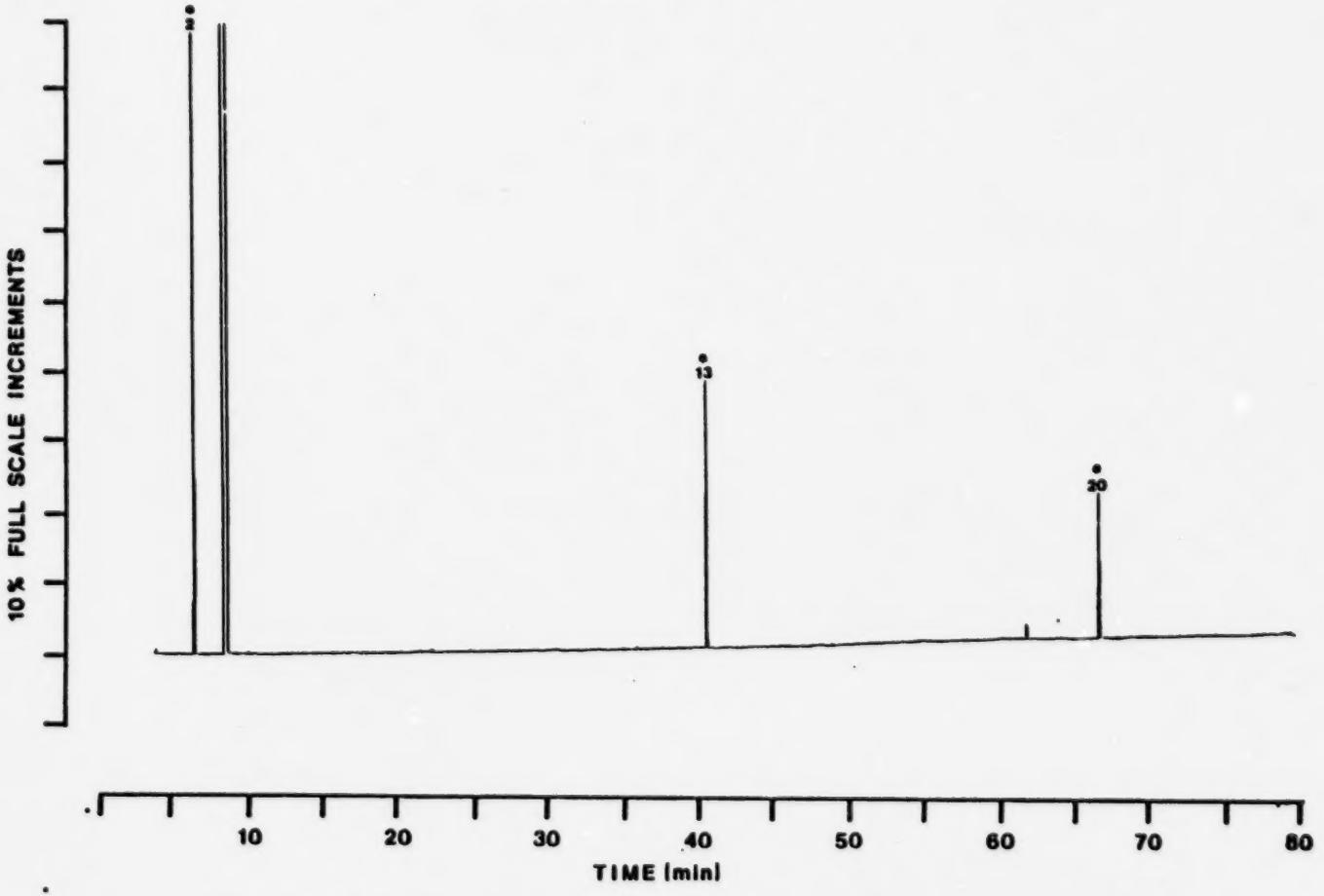

Figure 7. Chromatogram of extract of pesticide waste R3236 (see Table 2 for conditions); asterisk denotes internal standard.

TABLE 10. RESULTS OF ANALYSIS OF PESTICIDE WASTE BML-10-07-04A[a]

Identified analyte[c]	mg Analyte/g Waste[b] Mean	% RSD
p-xylene	3.0	46
o-xylene	3.2	20
2-chlorophenol	20	38
p-dichlorobenzene[d]	1.7	14
p-nitrophenol[d]	3.9	22
Methyl Parathion	609	48

a Six replicates.
b Mass of analyte divided by mass of waste extracted
c See Table 2 for chromatographic conditions.
d Questionable identification.

TABLE 11. RESULTS OF ANALYSIS OF PESTICIDE WASTE BDB-6-19-01A[a]

Identified analyte[c]	mg Analyte/g Waste[b]	
	Mean	% RSD
p-xylene	32.0	31
o-xylene	3.5	12

[a] Six replicates.
[b] Mass of analyte divided by mass of waste extracted.
[c] See Table 2 for chromatographic conditions.

TABLE 12. RESULTS OF ANALYSIS OF PESTICIDE WASTE BDB-6-19-02A[a]

Retention time (min)[c]	Normalized area ratio[b]	
	Mean	% RSD
51.9	0.322	28
53.3	2.17	25
58.6	0.418	31
63.4	0.964	30

a Six replicates.
b Computed from: (Peak area, compound/Peak area, int. std.) divided by weight of waste extracted; nearest eluting internal standard.
c See Table 2 for chromatographic conditions.

TABLE 13. RESULTS OF ANALYSIS OF PESTICIDE WASTE R3236[a]

Retention time (min)[c]	Normalized area ratio[b]	
	Mean	% RSD
8.8	6.1	10

a Six replicates.
b Computed from: (Peak area, compound/Peak area, I.S.) divided by weight of waste extracted; nearest eluting internal standard.
c See Table 2 for chromatographic conditions.

APPENDIX A

SOXHLET EXTRACTION PROCEDURE
METHOD 3540 (SW-846)

METHOD 3540

SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-mL round bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400°C for 30 min. or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr. in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 mL of the extraction solvent into a 500-mL round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4 inch column of sodium sulfate which has been washed with the

extracting solvent. Collect the dried extract in a 500-mL Kuderna-Danish (K-D) flask fitted with a 10-mL graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 mL of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the snyder column by adding about 1 mL solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain for at least 10 min. while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 mL with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical methods.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.